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(52) UK CL (Edition N)

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D21B D21X D51

G1A AA1 AA4 ABGX AR6 AR7

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Analytical Chemistry, Vol 58, No1, Jan 1986, pgs
97-105

(58) Field of Search

UK CL (Edition N) G1A ABGX, H1D DHBB DMAA

DMD DME DMG DMH

INT CL⁶ G01N, H01J

Online:WPI

(54) Analysis systems and processes

(57) An analysis system includes induction coupled plasma apparatus (28) into which sample material to be analyzed is introduced for excitation in the plasma, optical measuring apparatus (42) coupled to the induction coupled plasma apparatus (28) for analyzing the sample material, and mass spectrometer apparatus (54) also coupled to the induction coupled plasma apparatus (28) for analyzing the sample material. The mass spectrometer apparatus (54) includes a first region (76), a sampling member (56) adjacent the induction coupled plasma apparatus (28) that has an orifice through which at least some ions characteristic of the sample material may pass into the first region (76), a second region (78), and a gate valve (72) between the first and second regions (76, 78). The gate valve (72) is open when the analysis system is operating in mass spectrometer mode, and is closed when the system is operating only in optical measuring mode. Inert gas flows through the sampling member orifice towards the induction coupled plasma apparatus (28) from the first region (76) of the mass spectrometer (54) when the analysis system is operating in the optical measuring mode. It is possible to operate the analysis system in both modes simultaneously.

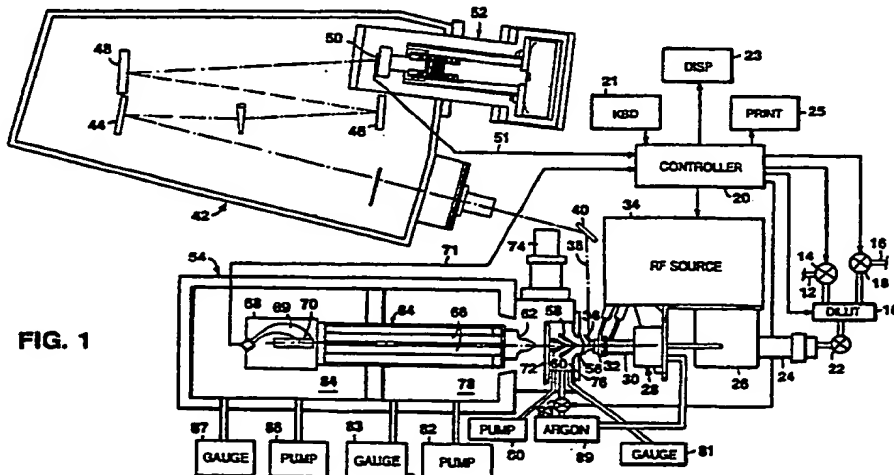


FIG. 1

GB 2 288 273 A

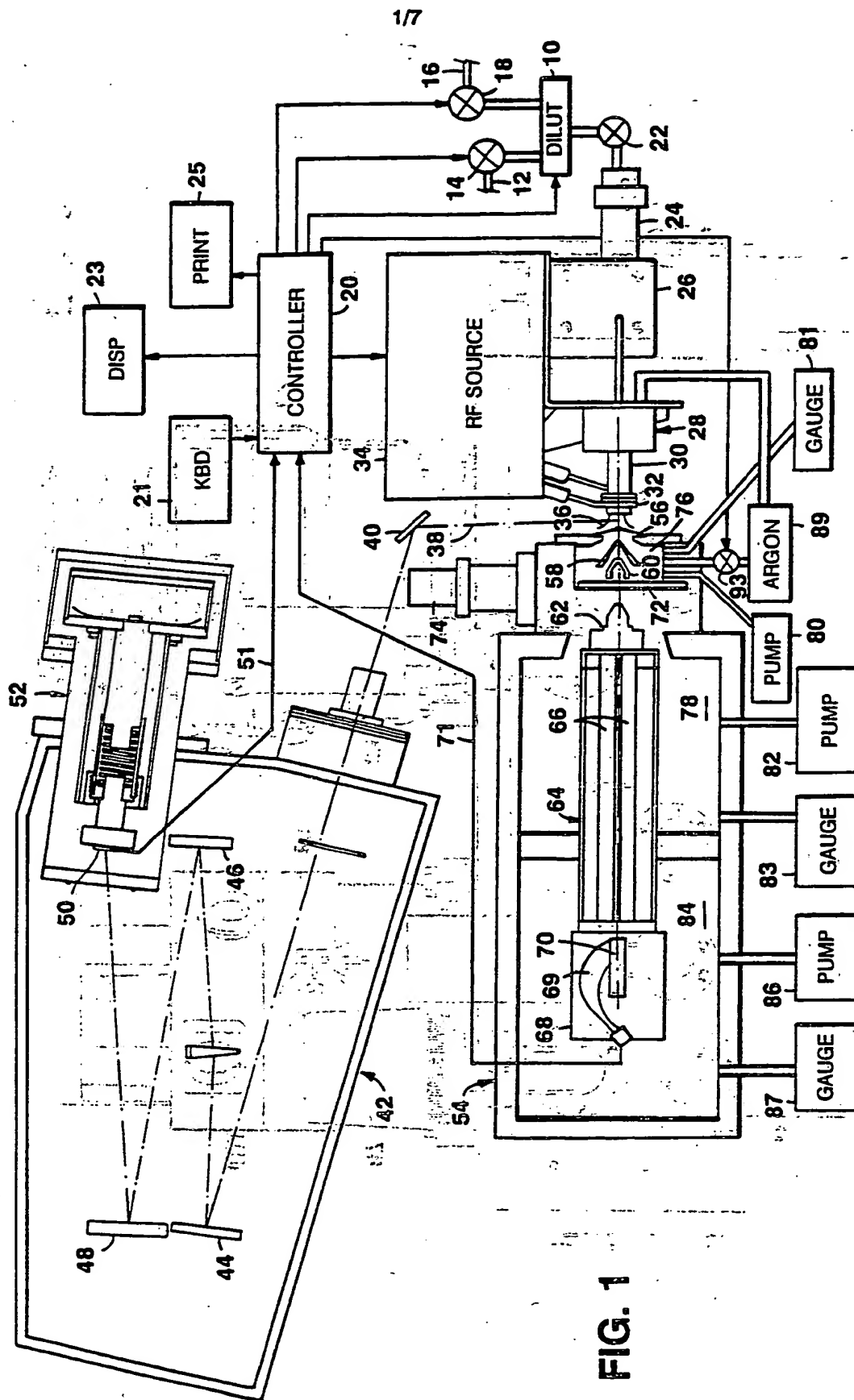


FIG. 1

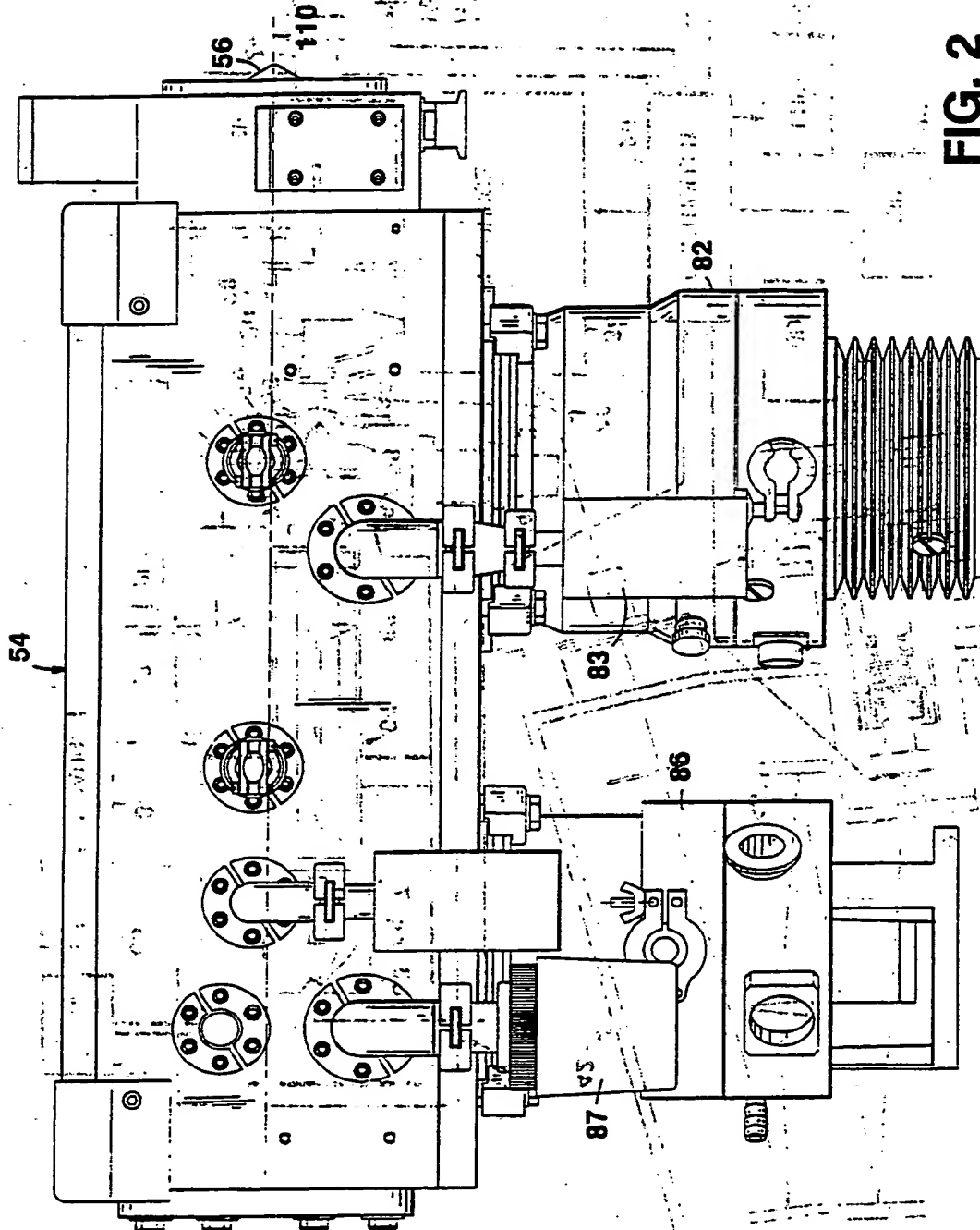


FIG. 2

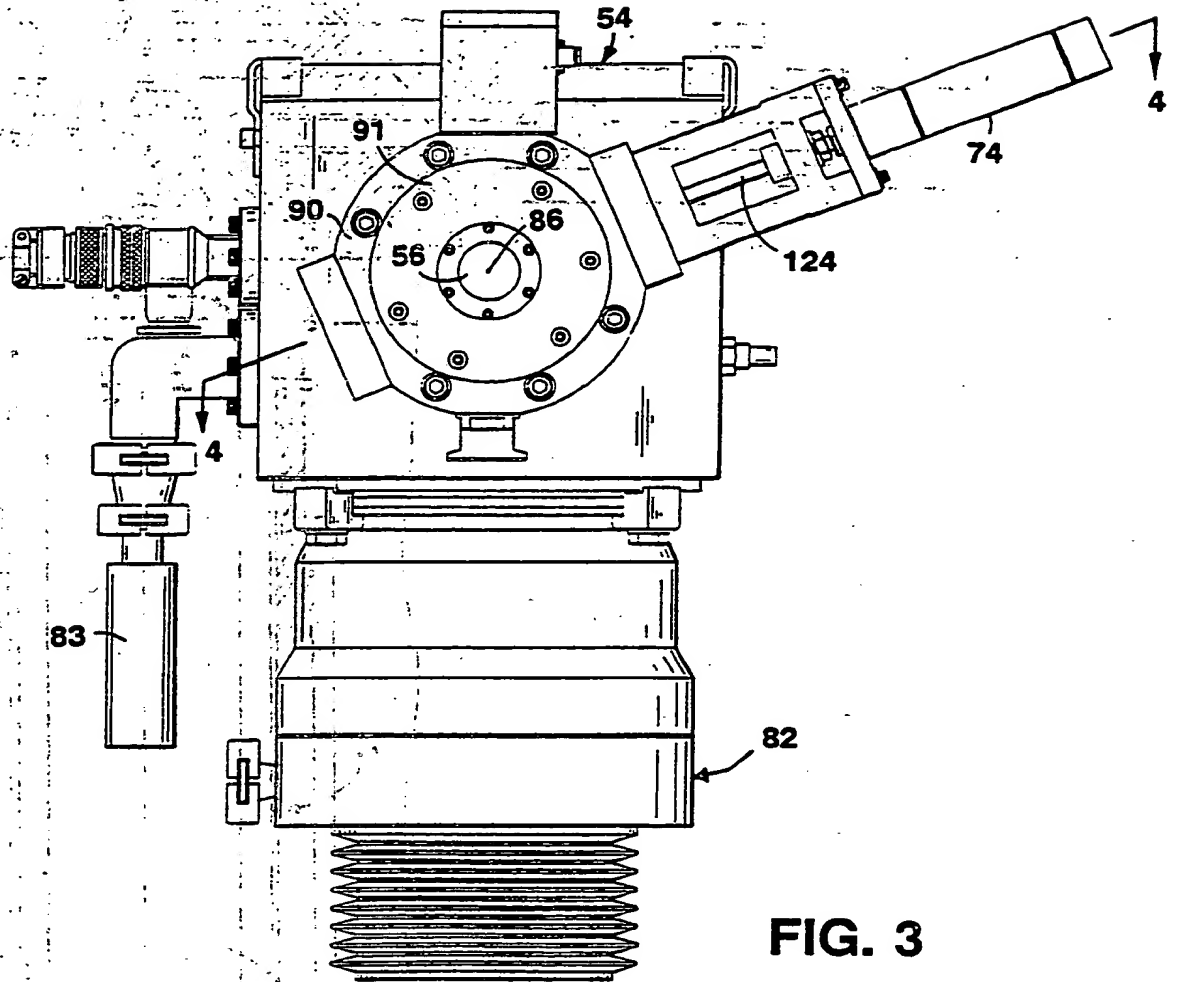
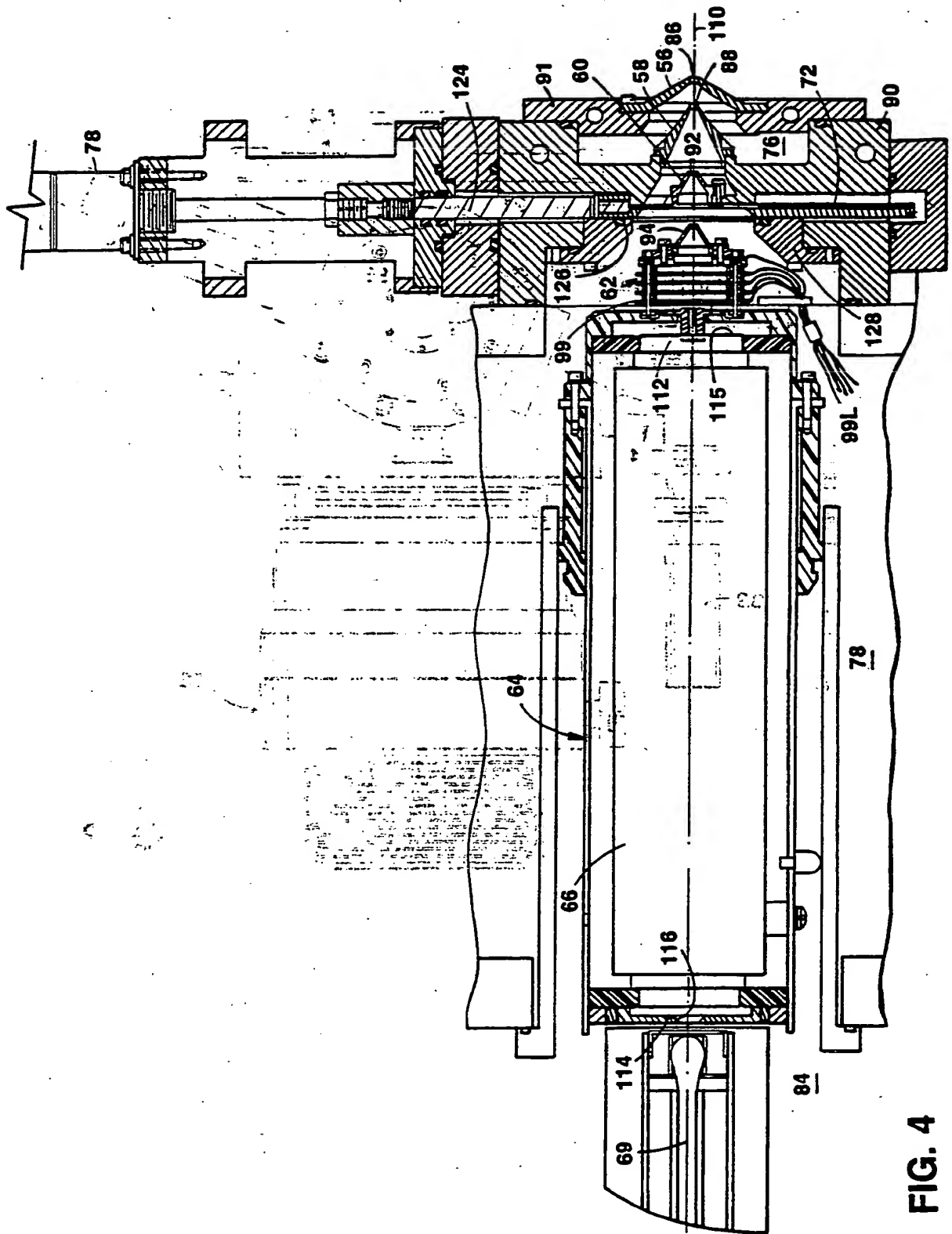


FIG. 3



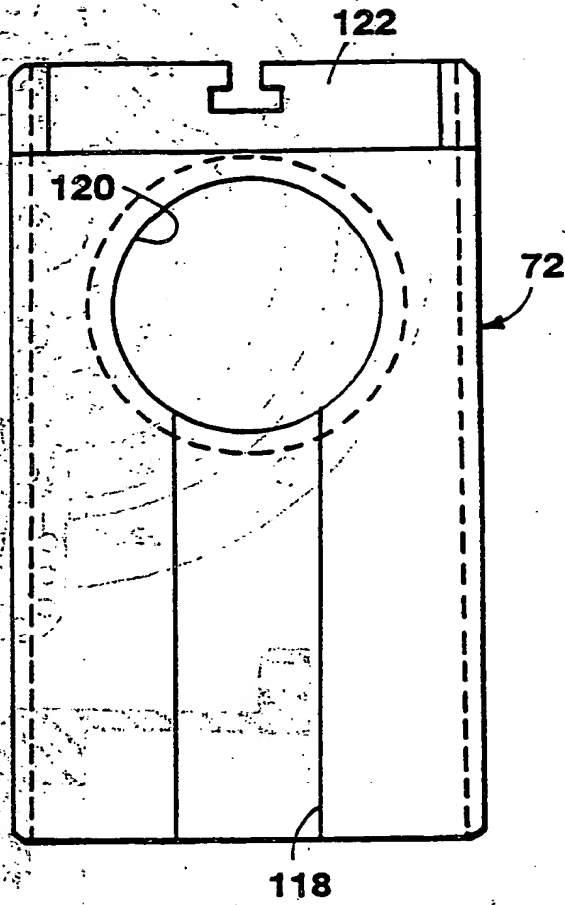


FIG. 5

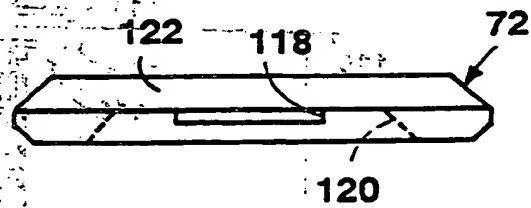


FIG. 6

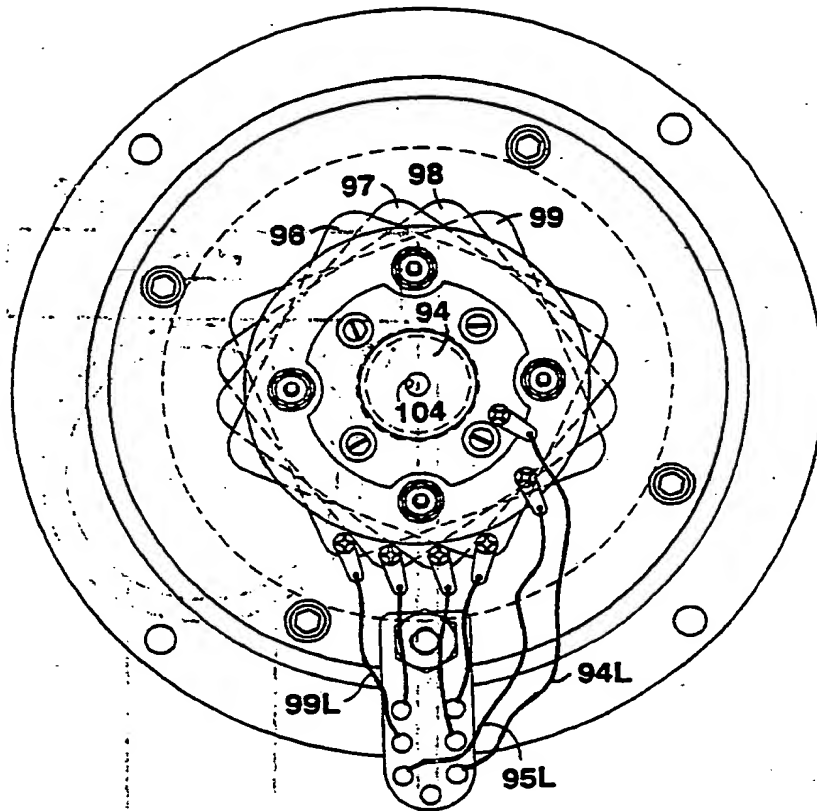
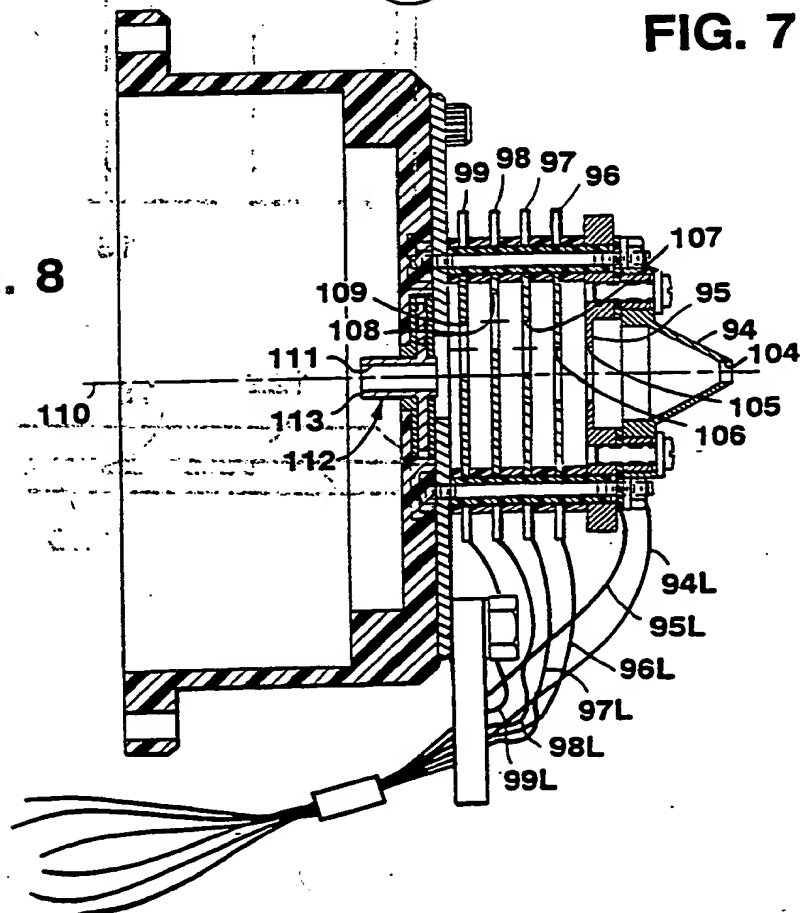


FIG. 7

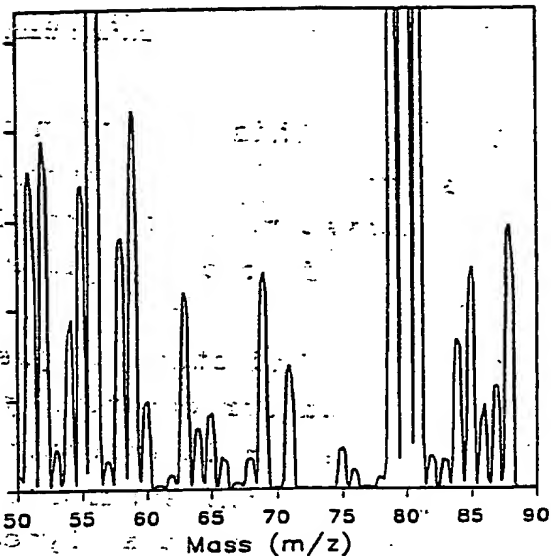
FIG. 8



10 ppb As, Co, Cr, Cu, Fe, Ga
Ni, Rb, Sr, V, Zn

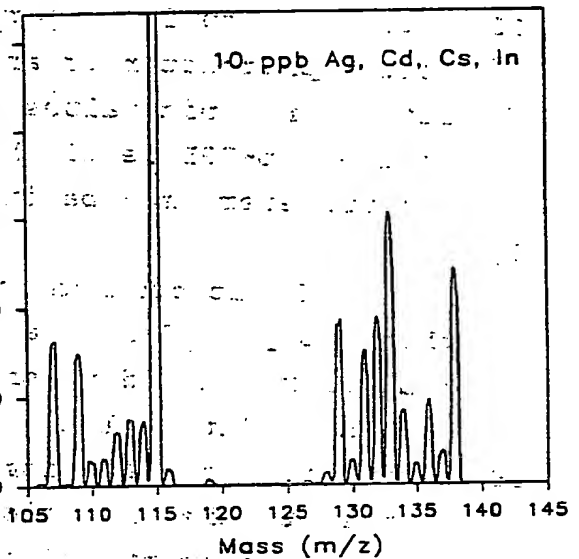
Count Rate
(counts s⁻¹)

FIG. 9A



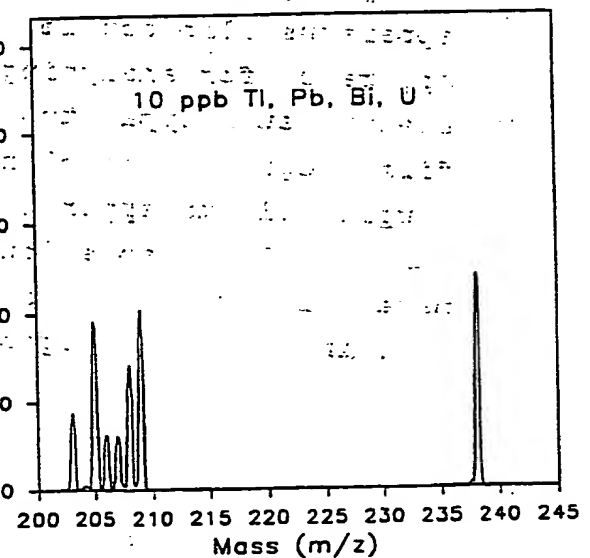
Count Rate
(counts s⁻¹)

FIG. 9B



Count Rate
(counts s⁻¹)

FIG. 9C



ANALYSIS SYSTEMS AND PROCESSES

5 This invention relates to analytical processes and systems, and more particularly to analytical processes and systems which are able to operate over a wide dynamic range of concentrations.

10 Induction coupled plasma devices have been employed for generating a high temperature plasma into which a sample solution to be analyzed is introduced for dissociation, atomization and ionization. The resulting material may be analyzed using a mass spectrometer or an
15 optical measuring apparatus such as an atomic absorption spectrophotometer or an emission spectrophotometer. Detection limit values of optical measuring apparatus are in the sub-PPB level while detection limit values of mass spectrometers may be in the PPT level.

20 In accordance with one aspect of the invention, there is provided an analysis system that includes induction coupled plasma apparatus into which a solution of sample material to be analyzed is introduced for
25 excitation in the plasma, optical measuring apparatus coupled to the induction coupled plasma apparatus for analyzing elements of the sample, and mass spectrometer apparatus also coupled to the induction coupled plasma apparatus for analyzing the sample material. The mass
30 spectrometer apparatus includes structure defining a first region, a sampling member adjacent the induction coupled plasma apparatus that has an orifice through which at least some ions characteristic of the sample material may pass into the first region, structure
35 defining a second region, pump structure coupled to the

second region for reducing the pressure in the second region below the pressure in the first region, valve structure disposed between the induction-coupled plasma apparatus and the second region, operator apparatus coupled to the valve structure for maintaining the valve open when the analysis system is operating in mass spectrometer mode, and maintaining the valve closed when the system is operating only in optical measuring mode. Preferably, the system includes structure for flowing an inert gas outwardly through the orifice towards the induction coupled plasma apparatus from the first region when the analysis system is operating in the optical measuring mode.

Preferably, ion lens structure is disposed in the first region immediately adjacent the valve structure, and a voltage in the range of -750 to -1,500 volts is applied to that ion lens structure; and the mass spectrometer includes a mass spectrometric separating system, ion detector apparatus, and focusing apparatus disposed between the source and the separating system, the focusing apparatus comprising an asymmetric electrostatic focusing lens system with a lens axis, an ion entrance aperture, an ion exit aperture and intermediate electrode structure disposed between the entrance and exit apertures having an aperture offset from the lens axis, and circuitry for applying a deflecting voltage to the intermediate electrode structure.

In a particular embodiment, the optical analysis apparatus includes a solid state detector with a two dimensional detector pixel array, and the system includes diluter structure for diluting the sample material introduced into the induction coupled plasma apparatus to a dissolved solids content of less than 0.2 percent.

In accordance with another aspect of the invention, there is provided a mass spectrometer with ion source structure for generating ions of a sample material to be analyzed, structure defining first and second regions adapted to be evacuated, sampling structure adjacent the ion source structure having an orifice through which at least some ions characteristic of the sample material may pass into the first region, focusing apparatus disposed in the first region, mass spectrometric separating apparatus disposed in the second region, ion detector apparatus coupled to the separating apparatus, and differential pumping structure between the first and second regions, the differential pumping structure having a tubular passage of at least five millimeters length and that extends into the second region with an exit port in overlapping relation to the separating apparatus so that ions are shielded from separating apparatus fringe magnetic fields and the stability of the magnetic field of the separating apparatus, particularly with respect to low mass (below 40) elements, is improved.

Preferably, the mass spectrometer separating apparatus includes a plurality of mass separation rods (that in a particular embodiment are quadrupole rods) and the exit port of the differential pumping structure is disposed within the entrance ends of the mass separation rods. The focusing apparatus comprises an asymmetric electrostatic focusing lens system disposed in front of the differential pumping structure with a lens axis, a conical electrode member that defines an ion entrance aperture, a planar electrode member that defines an ion exit aperture and an intermediate planar electrode member disposed between the entrance and exit apertures that has an aperture offset from the lens axis, and circuitry for applying deflecting voltages to the electrode members.

In a particular embodiment, the circuitry applies a voltage in the range of -750 to -1500 volts to the conical leading ion lens electrode member.

In accordance with another aspect of the invention, there is provided a mass spectrometer with ion source structure for generating ions of a sample material to be analyzed, structure defining first and second regions adapted to be evacuated, sampling structure adjacent the ion source structure having an orifice through which at least some ions characteristic of said sample material may pass into the first region, focusing apparatus disposed in the first region, mass spectrometric separating apparatus disposed in the second region, ion detector apparatus coupled to the separating apparatus, and exit lens structure between the separating apparatus and the detector apparatus. The exit lens structure has an entrance port of at least one centimeter diameter, an exit port of less than half the diameter of the entrance port, and passage structure that connects the entrance and exit ports, the passage structure having a length of at least five millimeters and being smoothly tapered for reducing background noise due to unwanted neutrals and photons.

In accordance with still another aspect of the invention, there is provided a mass spectrometer with an entrance axis, ion source structure for generating ions of a sample material to be analyzed for passage along the entrance axis, structure defining first and second regions adapted to be evacuated, sampler cone structure, skimmer cone structure, collection lens cone structure, focusing apparatus disposed in the first region, the focusing apparatus including ion lens cone structure. Each of the cone structures has an orifice and the orifices are disposed in series along the entrance axis. Mass spectrometric separating apparatus is disposed in

the second region, and ion detector apparatus is coupled to the separating apparatus. While it will be understood that other ion sources may be used as appropriate in other embodiments, in a particular embodiment, the ion source structure is inductively coupled plasma apparatus and an optically measuring spectrometer is coupled optically to the plasma apparatus. Valve structure is disposed between the collection lens cone structure and the ion lens cone structure. Operator apparatus is coupled to the valve structure and maintains the valve open when the analysis system is operating in mass spectrometer mode, and maintains the valve closed when the system is operating in only optical measuring mode. Structure flows an inert gas outwardly through the sampler and skimmer cone orifices towards the induction coupled plasma apparatus when the analysis system is operating only in the optical measuring mode. The optical analysis spectrometer includes a solid state detector with a two dimensional detector pixel array; and the system includes diluter structure for diluting the sample material introduced into the induction coupled plasma apparatus to a dissolved solids content of less than 0.2 percent for minimizing salt build-up on surfaces of the sampler and skimmer cone structures.

25 In accordance with another aspect of the invention, there is provided an analysis process that includes the steps of providing induction coupled plasma apparatus, optical analysis apparatus optically coupled to the induction coupled plasma apparatus for analyzing the sample material, mass spectrometer apparatus coupled to the induction coupled plasma apparatus for analyzing the sample material, diluter apparatus and controller structure introducing sample material to be analyzed into the induction coupled plasma apparatus, operating the diluter apparatus to dilute the sample material

introduced into the induction coupled plasma apparatus to a solids content of less than 0.2 percent; and using outputs from the induction coupled plasma apparatus and the optical analysis apparatus and the mass spectrometer apparatus to analyze the sample material.

Preferably, the mass spectrometer apparatus includes structure defining a first region, a sampling member adjacent the induction coupled plasma apparatus that has an orifice through which at least some ions characteristic of the sample material may pass into the first region, structure defining a second region, pump structure coupled to the second region for reducing the pressure in the second region below the pressure in the first region, and valve structure disposed between the induction coupled plasma apparatus and the second region, and the process further including the steps of maintaining the valve structure in open position when the analysis process is operating in mass spectrometer mode and maintaining the valve structure in closed position when the process is operating only in optical analysis mode; and the step of flowing an inert gas from the first region outwardly through the orifice towards the induction coupled plasma apparatus when the valve structure is in closed position.

The system and process provides versatility and flexibility, the mass spectrometer has excellent detection limits, improved sensitivity, low background and low interferences, and the optical analysis spectrometer extends the analysis range of the system and process.

Other features and advantages of the invention will be seen as the following description of a particular embodiment progresses, in conjunction with the drawings, in which:

Fig. 1 is a diagrammatic view of an analysis system in accordance with the invention:

Fig. 2 is a side view of mass spectrometer apparatus employed in the system of Fig. 1;

5 Fig. 3 is an end view of the mass spectrometer apparatus shown in Fig. 2;

Fig. 4 is a sectional view taken along the line 4-4 of Fig. 3;

10 Fig. 5 is a front elevational view of a gate valve member employed in the mass spectrometer shown in Fig. 4;

Fig. 6 is an end view of the gate valve member shown in Fig. 5;

Fig. 7 is a front view of the ion lens assembly employed in the embodiment shown in Fig. 4;

15 Fig. 8 is a sectional view taken along the line 8-8 of Fig. 7; and

Figs. 9a - 9c are diagrams indicating mass spectra obtained with the system shown in Fig. 1;

20 The analysis system shown in Fig. 1 includes diluter 10, with sample inlet 12 through piston pump 14, and deionized water inlet 16 through piston pump 18. Pumps 14, 18 are connected to controller 20 and the output of diluter 10 is connected through peristaltic
25 pump 22 to cross flow nebulizer 24 and spray chamber 26 that is connected to plasma torch assembly 28 for introducing sample material solutions to be analyzed into tube 30 of torch assembly 28. Coupled to controller 20 are input keyboard 21, display 23 and printer 25.
30 Surrounding tube 30 is induction coil 32 that is coupled to two kilowatt crystal controlled 27.12 megahertz RF generator 34. The sample material is excited to spectroemissive levels in plasma 36 and a beam 38 of radiation from plasma 36 is reflected by mirror 40 into

echelle spectrograph 42 for reflection by collimating mirror 44 and dispersion by echelle grating 46 and reflection by mirror 48 for sensing by solid state (CID) detector 50 that includes an array of 388X244 detector pixels, and that is coupled to dewar 52 for cooling detector 50, and that provides an output over line 51 to controller 20. Spectrograph 42 operates over a wavelength range of 190 - 900 nanometers, and is of the type shown in Smith U.S. Patent 5,088,823, the disclosure of which is expressly incorporated herein by reference.

Also coupled to the output plasma 36 is mass spectrometer 54 whose structure is shown in more detail in Figs. 2-8. Mass spectrometer 54 includes sampling cone 56, skimmer cone 58, collection lens 60, ion lens assembly 62, quadrupole mass analyzer 64 that includes four hyperbolic Invar rods 66; and detector system 68 that includes electron multiplier 69 and deflector 70 and that is coupled over line 71 to controller 20. Gate valve 72 is disposed between collection lens element 60 and ion lens assembly 62 (between expansion chamber 76 and ion lens chamber 78) and is operated by pneumatic cylinder 74.

When the analysis system of Fig. 1 is operating in mass spectrometer mode, gate valve 72 is open and ions characteristic of the sample material and present in plasma 36 enter mass spectrometer 54 through orifice 86 (Fig. 4) of sampling cone 56. Expansion chamber 76 is pumped by rotary pump 80 at a pumping speed of about ten liters per second to provide a pressure of about three torr in chamber 76 as monitored by thermo-couple gage 81; ion lens chamber 78 is pumped by turbo pump 82 at a pumping speed of 500 liters per second to maintain a pressure of about 3×10^{-4} torr in chamber 78 as monitored by pirani gauge 83; and quadrupole and detector chamber 84 is pumped by turbomolecular pump 86 at a pumping speed

of 400 liters per second to maintain a pressure of about 2×10^{-6} torr in chamber 84 as monitored by magnetron gage 87.

When the analysis system is operating in emission spectrograph mode, gate valve 72 is closed and argon from argon source 89 (as controlled by controller 20 and valve 93) is flowed from expansion chamber 76 out through orifices 88, 86 (Fig. 4) of skimmer cone 58 and sampling cone 56 at a rate of about one liter per minute to minimize salt buildup on surfaces of cones 56, 58. One or more major elements such as sodium, potassium, calcium or iron are monitored and controller 20 operates diluter 10 to control the dilution of the sample to a dissolved solids content of the sample less than 0.2 percent. The system can also be run in emission and mass spectrometer modes simultaneously (as with samples of known low dissolved solids content such as rain water or a pure acid) but the orifice protection feature is not used during such simultaneous operation as gate valve 72 is open.

With reference to Fig. 4, sampling cone 56, skimmer cone 58, collection lens 60 and the first ion lens electrode 94 are conical members of nickel and are disposed in sequence with their orifices on the entrance axis 110 of mass spectrometer 54. The diameter of sampler cone orifice 86 is 1.2 millimeter and the diameter of skimmer cone orifice 88 is one millimeter. The distance between orifices 86, 88 is about eight millimeters. Sampling cone 56 is mounted on water cooled copper face plate 91, and skimmer cone 56 is mounted on water cooled copper flange 90. Collection lens 60 has orifice 92 of about 1.2 millimeters, the next ion lens electrode 94 has orifice 104 of three millimeters diameter and the distance between collection lens 60 and the conical next ion lens electrode 94 is about eight

millimeters. Gat valve 72 is disposed between cones 60 and 94. Ion lens electrodes 95-99 (see also Fig. 8) are 1/2 millimeter thick stainless steel plates that are separated by spacer insulators and to which separate
5 voltages are applied over lines 95L-99L. Each collection lens plate 95-99 has an orifice 105-109 of about six millimeters diameter with orifices 105 and 106 on axis 110, orifices 107 and 109 being offset about three millimeters from axis 110, and orifice 108 being offset
10 about seven millimeters from axis 110.

Between the ion lens assembly 62 and the quadrapole chamber 64 is differential pumping orifice member 112 that defines a cylindrical passage 111 that is about eight millimeters long and about three millimeters
15 diameter with its exit port 113 disposed within and overlapping the entrance ends 115 of quadrapole rods 66 to shield ions exiting from passage 111 from quadrapole fringe magnetic fields and to improve the stability of the quadrapole magnetic field, particularly with respect
20 to low mass (below 40) elements. Disposed in quadrapole chamber 64 are four, 250 millimeter long hyperbolic Invar rods 66 that define an R_0 of twelve millimeters. Ions leaving the quadrapole chamber 64 are focused through eight millimeter thick aluminum exit lens 114 (Fig. 4)
25 that has conically-tapered through passage 116 that has an entrance diameter of thirteen millimeters and an exit diameter of five millimeters and are detected by a Channeltron Model 4870 electron multiplier 69. For maximizing transmission of $^{115}\text{In}^+$, the voltage applied to
30 collection lens 60 was -1,000 volts; to ion lens 94 was -100 volts; to ion lens 95 was -25 volts; to ion lens 96 was +30 volts; to ion lens 97 was -150 volts; to ion lens 98 was +30 volts; to ion lens 99 was -50 volts; to exit lens 114 was -115 volts; deflector 70 has a deflection
35 voltage of +10 volts applied to it; and electron

multiplier 69 has a voltage more positive than -2500 volts applied to it when operating in analog mode and a voltage more negative than -3000 volts when operating in pulse counting mode.

5 With reference to Figs. 5 and 6, gate valve 72 is a stainless steel plate about six centimeters wide, about eleven centimeters long, and about 0.4 centimeter thick. Recess 118 extends from port 120 and has a width of about two centimeters and a depth of one millimeter. Port 120 10 has a diameter of about 3.5 centimeters. Coupling structure 122 connects gate valve 72 to actuator 74 through connecting rod 124. Seal ring 126 is seated in clamp ring 128 and provides a seal when the pressure in ion lens chamber 78 is less than the pressure in 15 expansion chamber 76. As indicated above, when the analysis system is operating only in optical emission mode, gate valve 72 (port 120) is closed and maintained in a closed position and argon from source 89 is flowed from expansion chamber 76 through orifices 88, 86 at a 20 rate of about one liter per minute to reduce orifice contamination. When the gate valve 72 is to be moved, the pressure in chamber 76 is decreased to about three torr, allowing freer movement of the gate valve 72.

Mass spectra (plots of counts versus mass-to-charge ratio) obtained with the system in mass 25 spectrometer mode (gate valve 72 open), of 10 ppb As, Co, Cr, Cu, Fe, Ga, Ni, Rb, Se, Sr, V and Zn ions are shown in Fig. 9a; mass spectra of 10 ppb Ag, Cd, Cs, and In ions are shown in Fig. 9b; and mass spectra of 10 ppb Bi, 30 Pb, Tl, and U ions are shown in Fig. 9c.

The sensitivities and detection limits obtained with this mass spectrometer are listed in the following Table:

35. Element	Sensitivity (counts s ⁻¹ /mg L ⁻¹)	Detection Limits (ng L ⁻¹)
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⁷ Li	3.20×10^7	2
⁵⁹ Co	6.71×10^7	1
⁸⁹ Y	6.47×10^7	0.7
¹⁰⁹ Ag	3.01×10^7	1
5 ¹³³ Cs	5.20×10^7	1
¹⁵⁹ Tb	6.23×10^7	0.4
²⁰⁸ Pb	2.68×10^7	1
²⁰⁹ Bi	5.43×10^7	0.5
²³⁸ U	6.13×10^7	0.3

10 While a particular embodiment of the invention has been shown and described, various modifications will be apparent to those of ordinary skill in the art, and therefore, it is not intended that the invention be limited to the disclosed embodiment, or to details thereof, and departures may be made therefrom within the spirit and scope of the invention.

CLAIMS:

1. An analysis system comprising:
induction coupled plasma-apparatus,
5 structure for introducing sample material to be
analysed into said induction coupled plasma apparatus,
optical analysis apparatus optically coupled to
said induction coupled plasma-apparatus for analysing
said sample material, and
10 mass spectrometer apparatus coupled to said
induction coupled plasma apparatus for analysing said
sample material,
said mass spectrometer apparatus including
structure defining a first region, a sampling member
15 adjacent said induction coupled plasma apparatus and
having an orifice through which at least some ions
characteristic of said sample material may pass into
said first region, structure defining a second region,
pump structure coupled to said second region for
20 reducing the pressure in said second region below the
pressure in said first region, characterised by the
provision of valve structure disposed between said
induction coupled plasma apparatus and said second
region, and operator apparatus coupled to said valve
25 structure for maintaining said valve structure in open
position when said analysis system is operating in
mass spectrometer mode and for maintaining said valve
structure in close position when said system is
operating only in optical analysis apparatus mode.

30

2. The system of claim 1 wherein said valve
structure includes gate valve structure disposed
between said first and second regions.

35

3. The system of either claim 1 or 2 and

further including structure for flowing an inert gas outwardly from said first region through said orifice towards said induction coupled plasma apparatus when said valve structure is closed.

5

4. A mass spectrometer system comprising ion source structure for generating ions of a sample material to be analysed, structure defining first and second regions adapted to be evacuated, sampling structure adjacent said ion source structure having an orifice through which at least some ions characteristic of said sample material may pass into said first region, focusing apparatus disposed in said first region, mass spectrometric separating apparatus disposed in said second region, ion detector apparatus coupled to said separating apparatus, and differential pumping structure between said first and second regions, said differential pumping structure having a tubular passage and said passage extending into said second region with an exit port in overlapping relation to said separating apparatus.

5. The system of any preceding claim wherein said mass spectrometer apparatus includes a mass spectrometric separating system, ion detector apparatus, and focusing apparatus disposed between said induction coupled plasma apparatus and said separating system, said focusing apparatus comprising an asymmetric electrostatic focusing lens system with a lens axis, an ion entrance aperture, an ion exit aperture and intermediate electrode structure disposed between said entrance and exit apertures having an aperture offset from said lens axis, and circuitry for applying a deflecting voltage to said intermediate electrode structure.

35

6. The system of any one of claims 1 to 3 and 5 and further including mass spectrometer differential pumping structure between said first and second regions, said differential pumping structure having a tubular passage and said passage extending into said second region with an exit port in overlapping relation to said separating apparatus.

7. The system of either claim 4 or claim 6 wherein said separating apparatus includes a plurality of mass separating rods and said exit port of said differential pumping structure is disposed within the entrance ends of said mass separating rods.

8. The system of any preceding claim and further including exit lens structure between said separating apparatus and said detector apparatus, said exit lens structure having an entrance port, an exit port of less than half the diameter of said entrance port, and passage structure connecting said entrance and exit ports, said passage structure being smoothly tapered for reducing background noise due to unwanted neutrals and photons.

9. The system of any preceding claim wherein said mass spectrometer apparatus has an entrance axis and further including sample cone structure, skimmer cone structure, collection lens cone structure and ion lens cone structure, each said cone structure having an orifice and said orifices being disposed on said entrance axis.

10. The system of any preceding claim wherein said optical analysis apparatus includes a solid state detector with a two dimensional detector pixel array.

11. The system of any preceding claims and further including diluter apparatus and controller structure for operating said diluter apparatus to dilute the sample material introduced into said induction coupled plasma apparatus to a solids content
5 of less than 0.2 percent.

12. An analysis process comprising the steps of providing induction coupled plasma apparatus,
10 optically coupling optical analysis apparatus to said induction coupled plasma apparatus for analysing said sample material,
coupling mass spectrometer apparatus to said induction coupled plasma apparatus for analysing said
15 sample material,
providing diluter apparatus and controller structure for introducing sample material to be analysed into said induction coupled plasma apparatus,
operating said diluter apparatus to dilute the
20 sample material introduced into said induction coupled plasma apparatus to a solids content of less than 0.2 percent; and
sensing outputs from said induction coupled plasma apparatus with said optical analysis apparatus
25 and said mass spectrometer apparatus to analyse said sample material.

13. The process of claim 12 wherein said mass spectrometer apparatus includes structure defining a
30 first region, a sampling member adjacent said induction coupled plasma apparatus that has an orifice through which at least some ions characteristic of said sample material may pass into said first region, structure defining a second region, pump structure
35 coupled to said second region for reducing the

pressure in said second region below the pressure in
said first region, characterised by the steps of
providing valve structure disposed between said
induction coupled plasma apparatus and said second
5 region, maintaining said valve structure in open
position when said analysis process is operating in
mass spectrometer mode and maintaining said valve
structure in closed position when said process is
operating only in optical analysis mode.

10 14. The process of claim 13 characterised by the
further step of flowing an inert gas from said first
region outwardly through said orifice towards said
induction coupled plasma apparatus when said valve
15 structure is in closed position.

Patents Act 1977

Examiner's report to the Comptroller under Section 17

(The Search report)

Application number

GB 9506355:8

Relevant Technical Fields

(i) UK Cl (Ed.N) G1A (ABGX); H1D (DHBB, DMAA, DMG, DMH)

(ii) Int Cl (Ed.6) G01N, H01J

Search Examiner

M J DIXON

Date of completion of Search

27 APRIL 1995

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications

(ii) ONLINE: WPI

Documents considered relevant following a search in respect of Claims :-

1-3

Categories of documents

X: Document indicating lack of novelty or of inventive step.

P: Document published on or after the declared priority date but before the filing date of the present application.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

A: Document indicating technological background and/or state of the art.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
A	GB 2267994 A (FISONS) see Figure 1	1
A	GB 2219432 A (MAX-PLANCK) see Figure 1	1
A	GB 2176649 A (MAX-PLANCK) see Figure 1	1
A	US 4955717 A (GEOCHEMICAL SERVICES) see especially column 5, lines 17 to 25	1

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

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Patents Act 1977: SECOND SEARCH
Examiner's report to the Comptroller under Section 17
(The Search report)

Application number
GB 9506355.8

Relevant Technical Fields

Search Examiner
MR M J DIXON

(i) UK Cl (Ed.N) H1D (DHBB, DMAA, DMD, DME, DMG, DMH)

(ii) Int Cl (Ed.6) H01J (49/02, 49/06, 49/24)

Date of completion of Search
5 JULY 1995

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE: WPI

Documents considered relevant following a search in respect of Claims :-
4 AND DEPENDENT CLAIMS

Categories of documents

- X:** Document indicating lack of novelty or of inventive step. **P:** Document published on or after the declared priority date but before the filing date of the present application.
- Y:** Document indicating lack of inventive step if combined with one or more other documents of the same category. **E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.
- A:** Document indicating technological background and/or state of the art. **&:** Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
Y	GB 1515406 A (EXTRANUCLEAR) see shielding tube 17	4, 7, 9
Y	GB 1460634 A (EXTRANUCLEAR) see especially tubes 17, 21, 22 and 29, Figures 1 and 3	4, 7, 9
Y	GB 1242031 A (HEWLETT-PACKARD) see conical tubes 52, 54	4, 7, 9
Y	Analytical Chemistry, Vol 58, No 1, January 1986, pages 97-105 R.S. Hook, "Mass spectrometry of Inductively Coupled Plasmas", see especially Figure 3a	4, 7, 9

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

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Patents Act 1977 THIRD SEARCH
Examiner's report to the Comptroller under Section 17
(The Search report)

Application number
 GB 9506355.8

Relevant Technical Fields

(i) UK Cl (Ed.N) G1A (ABGX); H1D (DHBB, DMAA, DMG, DMH)

(ii) Int Cl (Ed.6) G01N; H01J

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE: WPI

Search Examiner
 MR M J DIXON

Date of completion of Search
 5 JULY-1995

Documents considered relevant following a search in respect of Claims :-
 12-14

Categories of documents

- X: Document indicating lack of novelty or of inventive step. P: Document published on or after the declared priority date but before the filing date of the present application.
- Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.
- A: Document indicating technological background and/or state of the art. &: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
A	US 4955717 A (GEOCHEMICAL SERVICES)-see especially column 5, lines 17-25	12

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